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The Detection and Study of Molecular Species  
Using Time Resolved Laser Spectroscopy

Final Report

by

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Department of Chemistry

July 1988

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>The detection of trace components in the atmosphere and contaminants or other active agents in or on support facilities is of primary importance to the protection of military personnel. One proposed approach relies upon the decomposition of the agent followed by the detection of characteristic fragments. This allows highly sensitive, remote spectroscopic techniques to be used for the analysis. In the design of propellents, it is important to be able to characterize and</b>		

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study their primary decomposition products. This also creates a need for the remote detection of molecular fragments, many of which are not well studied chemical species.

New laser spectroscopic techniques are being developed which will provide considerable advantage in both sensitivity and selectivity in the detection and identification of labile species. Several are based upon multiphoton ionization spectroscopy using pulsed laser sources and ion detection methods. Multiphoton ionization spectroscopy has the highest potential sensitivity of any analytical method. It can also be combined with mass spectral analysis and electron kinetic energy analysis. The result is a multidimensional mapping of the interaction between the laser excitation source and the system under study. While it may not be feasible to use such complex technology for field applications, the information obtained in the laboratory can be invaluable in the design of simpler methods for remote or point analysis for specific species.

The purpose of this basic research effort will be to identify and characterize small molecular fragments formed from the decomposition of model compounds. It is hoped that the results of such research will form the genesis for nondestructive, quantitative analysis methods under field conditions requiring either remote or point sensing.



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  - "Mass and Photoelectron Studies of UV-Multiphoton Fragmentation Processes in Molecules," S.D. Colson, NIM B27, 130 (1987).
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## Final Report

### UV-Multiphoton Fragmentation in Isolated Molecules

A major advance in the utility of laser spectroscopy came as a result of the development of multiphoton ionization MPI as a means of detection of multiphoton absorption by molecules[1]. The resonance encountered as the  $n$ -photon energy of a scanning laser becomes coincident with the energy of a molecular excited state is evidenced by a large increase in ionization rate. Since single ionization events can be detected with near unit efficiency, this results in a very sensitive means of detecting weak multiphoton absorption. MPI is a more widely applicable method than laser induced fluorescence LIF since it can be used for non-emitting states. Nevertheless, it was discovered in some of the earliest MPI studies[2] that the efficiency of the process was limited by the competition between MPI and multiphoton driven dissociation MPD to form neutral fragments. If properly understood, this process can be used to advantage in point and remote sensing of specific agents. Many chemical agents are highly complicated molecules and are difficult to uniquely identify optically because of their very complex spectra. However, specific agents will often be characterized by particular functional groups of atoms. If these functional groups can be liberated from the parent molecule (by laser driven dissociation) their smaller, simpler structure often leads to a means for highly sensitive, quantitative analysis.

The most striking finding resulting from the important union of MPI and mass spectrometric methods was that the molecular ions themselves also exhibited extensive photo-fragmentation. This resulted in the promulgation of an extensive body of experimental and theoretical work on laser fragmentation following ionization[3]. With the exception of organometallics, where neutral fragmentation dominates[4], the competition between neutral fragmentation and ionization was almost completely ignored until recently[5-7]. During the course of this work, it became apparent that the neutral channel dominates for many simple organic systems[5]. Thus, it is important to include fragmentation, both prior and subsequent to ionization, in any overall discussion of the multiphoton fragmentation process.

After the initial UV excitation, there will generally be two radiationless processes in competition with further absorption; relaxation (to another isocenergetic state of the parent) or fragmentation (to form daughter species). Each of these branching routes can also be followed by additional UV excitation, and the same branching is possible for each species formed by the absorption of the additional photon(s). After the threshold for ionization is exceeded, yet another competitive channel is opened. The result is a very complex tree of processes, especially when one considers that numerous distinct relaxation and/or fragmentation branches could emanate from a single excited state.

The modeling of MPD in molecules is complicated by the fact that there are often several pathways by which a particular fragment might be formed. To aid in the interpretation of the results from a

particular system, one generally has access to three variables, the laser wavelength, its pulse width, and its intensity. Because the photo-driven processes can be very strongly dependent upon intensity, the overall result can often be dramatically altered by simply changing the intensity (see Fig. 1 [8]). The reason for the frequent neglect of neutral fragmentation is the difficulty in detection of the neutral fragments. If an appropriate wavelength is used for the detection of these fragments, they are often found in great abundance. Fig. 2 shows an example where the absorption of the parent molecule is sufficiently broad that the laser wavelength can be scanned to simultaneously drive the MPD process and show the MPI spectrum of the photofragments [9]. In general it will be necessary to use more than one laser simultaneously to independently pump the parent absorption and probe for fragments. The time evolution of the various processes can be studied either by varying the laser pulse width (Fig. 3) or the time delay between pump and probe lasers [10] (Fig. 4).

Of primary interest is the mechanism by which a molecule is driven to a sufficiently high level of excitation to result in extensive fragmentation. One might envision three limiting cases; 1) absorption of  $n$ -photons by the parent molecule followed by a concerted fragmentation into a statistical distribution of products, 2) absorption of  $n$ -photons by the parent followed by a sequential series of dissociations involving metastable fragments, or 3) a series of one or two photon driven dissociation steps wherein the daughter species absorb at the same frequency as the parent.

The concerted fragmentation of a large polyatomic is unlikely. In the case of acetone, for example, the one-photon, UV photolysis to produce two methyl radicals and CO is found to involve a metastable acetyl fragment [11]. Statistical models which neglect differential absorption cross sections of the fragments (which should be apparent if case-3 were operative) have achieved reasonable success in describing ion photofragmentation processes [3]. This is true even for cases where the extent of the fragmentation requires absorption of two or three photons after passing the first dissociation threshold.

The MPI/MPD of butadiene provides an excellent example of case-2 multiphoton photodissociation [8]. This is a two laser experiment where one laser is used to prepare the ion in its ground state and the other is used to study its fragmentation. The lasers are operated with pulse widths of about 10 ns with the fragmentation laser arriving 12 ns after the ionization pulse. The wavelength of the ionization laser pumps the origin a selected intermediate Rydberg state resulting in the exclusive preparation of  $v=0$  ions as shown from the MPI photoelectron spectrum PES at this wavelength. At sufficiently low laser powers, the butadiene ion is formed with little additional fragmentation (Fig. 1). The fragmentation laser wavelength corresponds to the first absorption band in the ion. This absorption is observed to be very broad due to a rapid rate of internal conversion to the ground state of the ion. The energy of these ground state ions is insufficient to cause rapid fragmentation. However, the hot ions can absorb another photon by the same electronic transition as before. This will produce vibrationally and electronically excited ions which are expected to undergo internal conversion to the ground state at an even faster rate than before. This process can be repeated again and again, resulting in the cyclical pumping of the vibrational excitation into the ground electronic state of the ion in 20,200  $\text{cm}^{-1}$  increments.

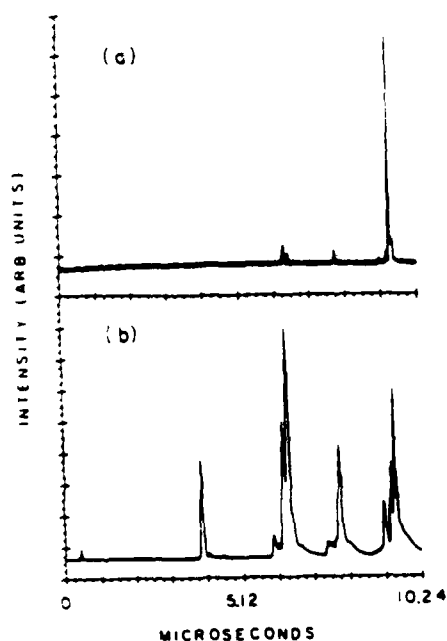


Figure 1. Time-of-Flight mass spectrum of butadiene at 399.1 nm at two different laser powers: (a) 90  $\mu$ J and (b) 800  $\mu$ J. (ref. 8)

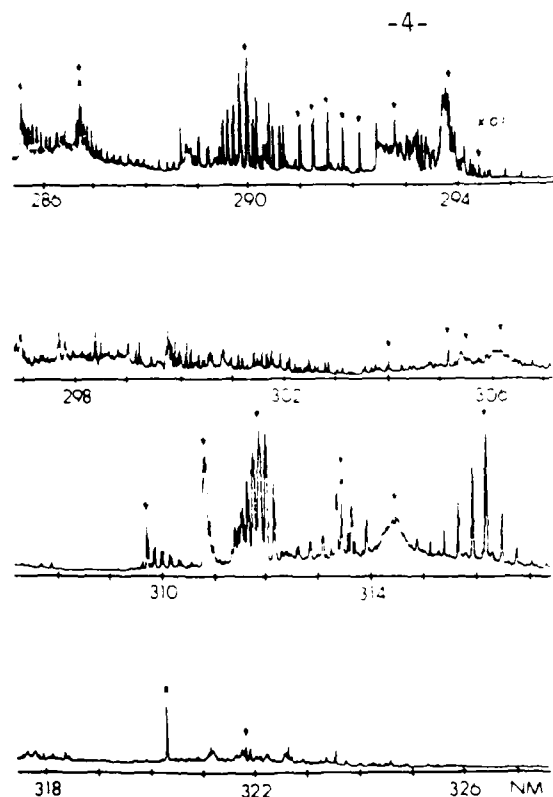


Figure 2. MPI-MS wavelength scans for  $m/e=13$  by resonant 2+1 MPI of CH produced by photodissociation of ketene. Arrows mark wavelengths at which photoelectron spectra have been taken. Asterisks mark peaks due to atomic carbon transitions appearing in the CH channel because of Coulomb broadening of the time-of-flight mass spectrum. (ref. 9)

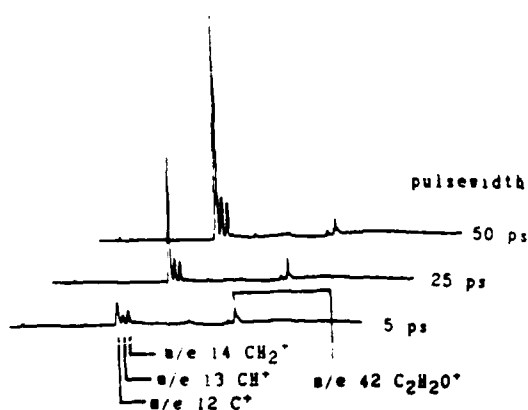


Figure 3. Production and subsequent ionization of atomic carbon from ketene using MPI-MS detection. The pulse width of the excitation laser was varied from 5 to 50 psec at constant pulse energy and at 331.6 nm. (ref. 12)

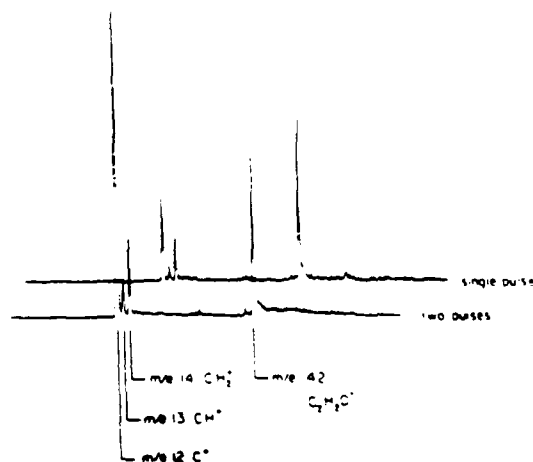


Figure 4. Same as Fig. 3 but showing the use of two 5 psec laser pulses delayed by 330 psec. (ref. 12)



The ion will continue to gain vibrational energy until the dissociation rate exceeds the absorption rate. By assuming a statistical distribution of the energy in the hot ions, RRKM theory calculations were made of the most rapid dissociation rates following absorption of one, two and three photons. These rates and the known ion breakdown curves[12] predict the fragmentation pattern shown in Fig. 5b. The excellent agreement with experiment (Fig. 5a) gives considerable credence to the cyclical pumping mechanism for creating high levels of vibrational excitation before dissociation. In the above case, at least half of the ions receive over  $60,000 \text{ cm}^{-1}$  of vibrational excitation before dissociation, nearly  $43,000 \text{ cm}^{-1}$  above the dissociation threshold. This mechanism is expected to be important in systems characterized by reasonably strong pumping of allowed transitions with rapid internal conversion back to the initial state. To prevent rapid dissociation above the first dissociation threshold, the excess energy must be distributed over a large number of vibronic states. Thus, larger molecules will be more susceptible to this type of pumping.

If all fragments which show secondary daughter species absorb equally strongly at the same frequency as the parent molecule, the main difference between cases 2 and 3 is kinetic. Case-3 presumes that dissociation is rapid compared to absorption. Thus, time resolved experiments are expected to provide a better understanding of the mechanism. Indeed, recent psec [9-13] and fsec [14] studies are proving to be very important in this regard.

The MPI/MPD of ketene is an excellent example of the combined use of MPI-MS to identify the photoproducts, MPI-PES to aid in the analysis of their spectra, and time-resolved spectroscopy to show the existence of case-3 processes. Ketene is photolyzed with a near UV, pulsed laser at the input of a time-of-flight mass spectrometer. The observed fragmentation is extensive; C and CH are observed directly,  $\text{CH}_2$ , CO and H or  $\text{H}_2$  are implied. By monitoring the various mass channels (e.g. C and CH), one obtains the convolution of their MPD excitation spectrum and their optical absorption spectrum detected by MPI. The results for the CH channel are shown in Fig. 2. Many of these bands are new and their analysis is greatly aided by obtaining the photoelectron spectrum at each of the wavelengths indicated in the figure. Since the upper states in these spectra are all Rydbergs with essentially the same geometry as the ion, vertical ionization results in simple PES spectra which can be used to provide upper state vibrational labels for all of the transitions shown in Fig. 2. This was especially helpful for overlapping bands which can be unscrambled by this vibrational labeling technique as seen in Fig. 6.

The one-photon absorption band in ketene is only weakly allowed and the molecule is small and rigid and is therefore not likely to result in cyclical pumping. Dissociation will probably occur before sufficient energy is absorbed to produce all of the observed fragments, e.g. case-3. The time resolved experiments of Chen, et al. [8] are consistent with this expectation. In this experiment, a sync-pumped dye laser is tuned into resonance with a two-photon atomic carbon transition. The carbon ion signal (due to  $2+1$  MPI of neutral carbon) increases as the pulse width of the laser is varied from 5 to 50 psec at constant energy (Fig. 3). This suggests that some molecular processes must precede the photoabsorptive event that produces the carbon atoms. This is confirmed by a two-pulse experiment where the psec laser is split into two beams of nearly equal intensity and recombined in the sample with a variable time

delay. In Fig. 4 it can be seen that the efficiency of carbon atom production is greatly enhanced by the time delay. From this we can conclude that, after the initial absorptive event, some dark process must precede the formation of carbon atoms, e.g. Case-3.

From the above discussion it can be seen that we have developed a powerful array of capabilities for the study of laser photolysis processes utilizing time resolved laser ionization spectroscopy with mass and photoelectron energy analysis. These capabilities can be utilized to study photodecomposition mechanisms in chemical agents and for the development of analytical methods specific to these agents. As an important spinoff of this research, the same methods can be used in the study of energetic materials and to obtain new spectroscopic data on transient species produced during their decomposition.

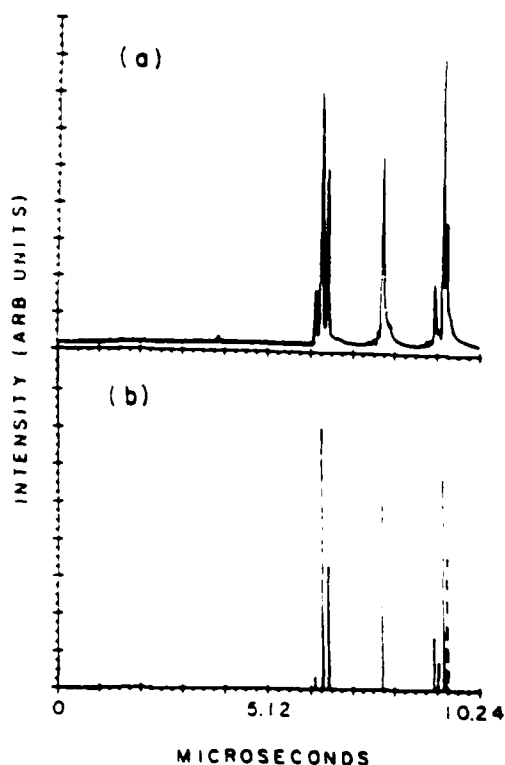


Figure 5. (a) Experimental two-laser TOF mass spectrum of butadiene photoionized at 399.1 nm and subsequently photodissociated at 495 nm. (b) Calculated spectrum obtained by using equal amounts of two- and three-photon absorption of the photodissociation laser. (ref. 8)

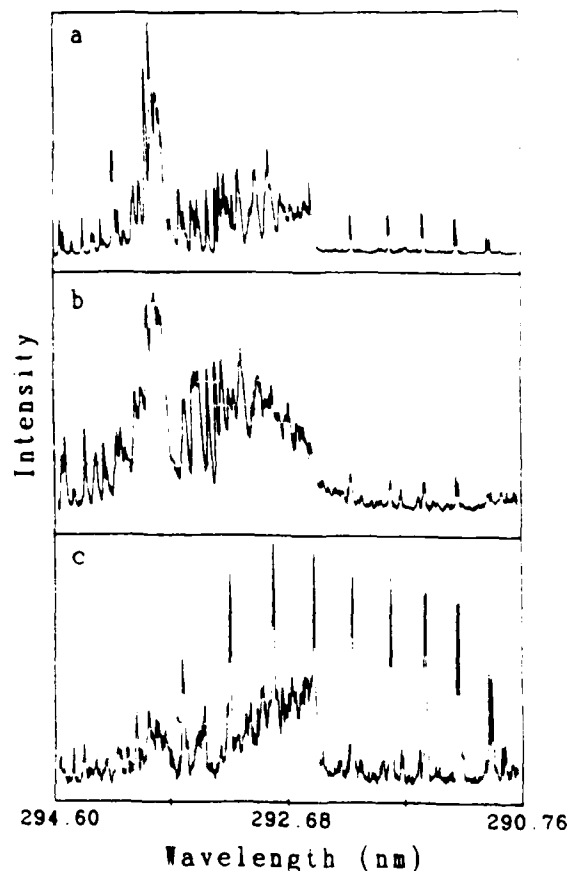


Figure 6. (a) Mass resolved ( $m/e=13$ ) wavelength scan of the production of neutral CH from the photodissociation of ketene. (b) and (c) Photoelectron energy resolved wavelength scans which monitor the intensity of the photoelectron peak corresponding to formation of the ground state of the CH ion in the  $v=1$  and  $v=2$  vibrational levels, respectively. The results in (b) and (c) show that there are two intermediate states with different vibrational quantum numbers which contribute to the overall CH ionization yield shown in (a).

## Flash Pyrolysis with Optical and Mass spectral Analysis

Pyrolysis provides another means for the decomposition of larger molecules (chemical agents or energetic materials) and their detection. The description of thermochemical reactions often requires suppositions about transient intermediate species about which there is little if any experimental data. During the course of this research, we have developed a pulsed pyrolysis nozzle for the study of these reactions. This new high temperature, pulsed nozzle (vide infra) is used to freeze thermochemical reactions at early stages of the reaction sequence by rapid expansion into vacuum and cooling to low temperatures (10-40 K)[15,16]. The "frozen" reaction mixtures are then available for spectroscopic analysis providing directly the mechanism as well as spectroscopic data on the intermediate species. This is in sharp contrast to most current methods wherein the existence of specific intermediates is only supported by the preparation of complex reaction schemes (involving 10-30 steps) which predict the correct final product ratios.

We find, for example, that the thermal decomposition of nitromethane involves very little rearrangement to methyl nitrite before decomposition to form nitrogen dioxide and methyl radicals (see Fig. 7) [16]. This is in direct contrast to theoretical calculations[17] but consistent with other less definitive experiments[18].

Our technique utilizes a time-of-flight TOF mass spectrometer with laser ionization to analyze the products of the thermal decomposition[15].

Depending upon the configuration of this source, we have a variety of new capabilities to utilize in this work. The nozzle can be configured to eliminate bimolecular reactions such that thermal reactions can be "frozen" after the initial step as illustrated in Figure 7. This is not only an important tool for the study of reaction mechanisms but also a valuable means for the preparation of specific species for spectroscopic study[15]. Alternatively, the nozzle can be configured to study bimolecular reactions at high temperatures, either preceding or subsequent to initial thermal decomposition reactions. Furthermore, by controlling the timing, gas pressure etc., we can vary the reaction time and observe directly the evolution of the sequential steps in the reaction. Each of these capabilities is important to the full understanding of thermal reactions under normal reaction conditions.

The pulsed pyrolysis valve is shown schematically in Figure 8. In the current design, the gas pulse is heated to ~1200 K. With some modifications, we expect to approach 1900 K. The 1 mm I.D. pyrolysis tube is loaded with a pulsed gas mixture at 1 to 10 atm by either a Lasertechnics or General valve with pulse widths variable from 100 sec. to >1 msec. Thusfar, we have only used samples with significant vapor pressures at room temperature. However, the device could be modified to allow injection of laser vaporized solid samples at the input of the hot tube. The pulse intensity is only limited by the pumping speed of the vacuum chamber which in our case (with a 10 inch CTI cryopump in a chamber whose walls are cooled with 77 K baffles) can maintain the pressure in the  $10^{-6}$  torr range for cw operation when using 1-2 atm of Ar carrier gas. When short (~100  $\mu$ sec) pulses are

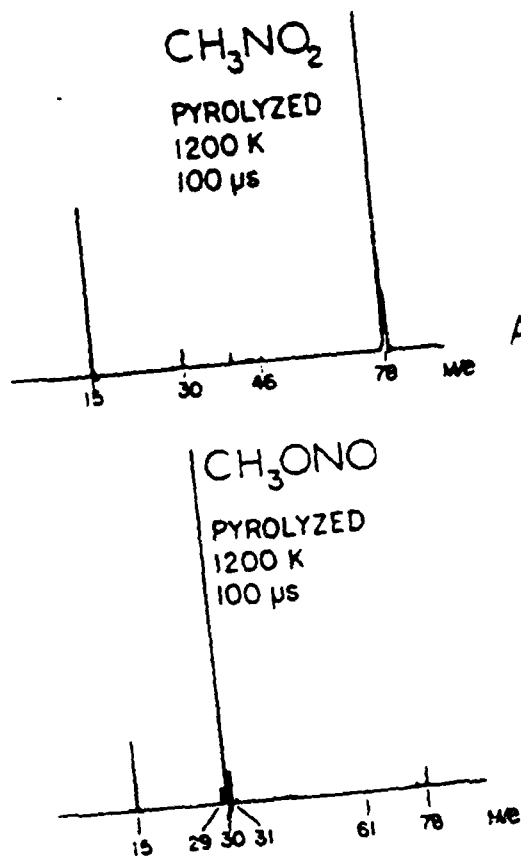


Figure 7. Time-of-Flight mass spectra of pyrolyzed nitromethane (a) and methyl nitrite (b), at <0.05% dilution in 2.5 atm argone and using 10.49 eV photoionization in a supersonic jet. The peak at  $m/e=78$  is benzene added as a mass calibrant. Mass spectra taken without pyrolysis show no ionization of nitromethane (I.P.=11.07 eV) and only parent ions at  $m/e=61$  from methyl nitrite (I.P.=10.37 eV). Ref. 19.

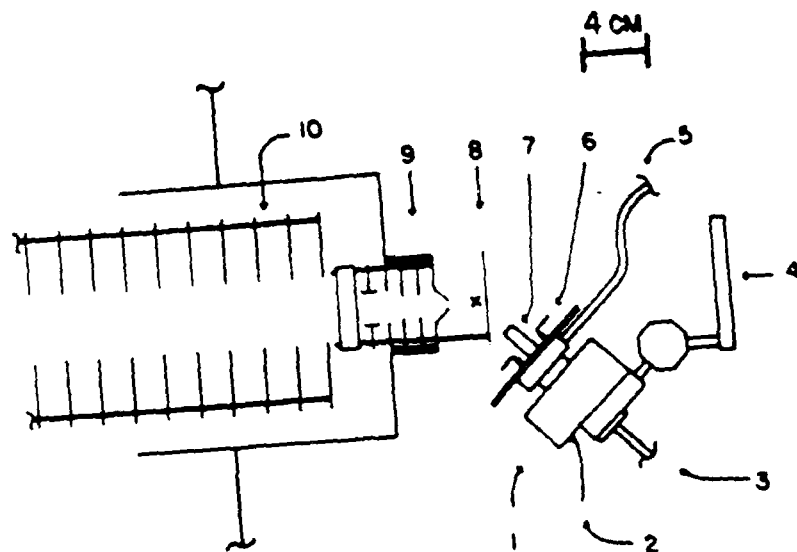


Figure 8. Source region of the time-of-flight mass spectrometer configured for the ionization of flash pyrolytically produced reactive intermediates, drawn to scale. Ionization laser crosses the supersonic jet perpendicular to the page at the point marked X. Differential pumping occurs across the skimmer. (1) pulsed valve with 500  $\mu$  orifice. (2) Electrical input pulse to valve. (3) Sample gas inlet. (4) Mounting bracket for Newport XYZ translation stage. (5) Cooling water inlet and outlet. (6) Electrical connector for pyrolysis tube filament; typically 15 W dc power. (7) Flash pyrolysis tube with heat shielding and grounded outer cage. (8) Ion repeller ring. (9) Ion optics stack. (10) Ion flight tube leading to electron multiplier.

injected into the pyrolysis tube, the gas dynamics are such that, except for the leading ( $\sim 20 \mu\text{sec}$ ) and trailing edges of the pulse, the entire gas sample shows uniform heating and there is no evidence for bimolecular reactions[14]. This capability can be used to study thermochemical reaction mechanisms and to obtain optical spectra of transient reaction intermediates.

By loading the heated tube with a lower intensity, longer gas pulse, we have been able to study bimolecular reactions of the thermochemical reaction products. Figure 9 shows the time evolution of the methyl signal as a function of time, measured from the beginning of the gas pulse which is injected into the hot tube. The sample consists of a few percent of nitromethane in an argon carrier gas. The methyl radicals formed during the first part of the gas pulse can react with the parent compound or  $\text{NO}_2$  to form  $\text{NO}$  and other products not detected at the ionization wavelength used in this experiment. Thus the ratio of methyl to  $\text{NO}$  decreases rapidly with time as shown in Figure 9[16]. This configuration can be used to study bimolecular reactions at high temperatures.

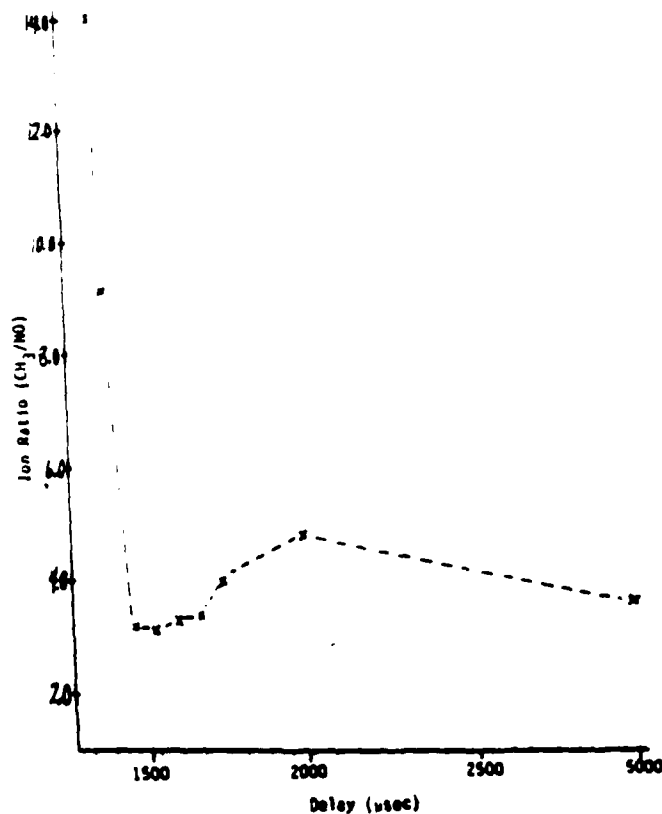


Figure 9. The  $\text{CH}_3^+/\text{NO}^+$  ratio vs the time delay between firing the pulsed valve and the ionization laser. The first point represents the leading edge of the gas pulse.

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